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Chief of Naval Research (Code 425)

Final Technical Report  
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Feb. 1, 1953 to Jan. 31, 1954

#### ANODES FOR PREPARATION OF ALKALI

##### PERCHLORATES

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## ANODES FOR PREPARATION OF ALKALI PERCHLORATES

### I. SUMMARY

The existing data about the equilibrium and over-voltages for the discharge of oxygen and the chlorate-perchlorate conversion at a smooth platinum anode are used to calculate the corresponding discharge potentials. It is found that perchlorate production is apparently one of those anomalous cases where the process associated with the higher voltage is the one which takes place. It is concluded that a theoretical approach to the perchlorate anode problem is not feasible due to the present state of development of electrochemical theory.

A final report on the exploratory research on the perchlorate anode problem performed at Horizons is made. While it was possible to prepare both magnetite and magnetite-coated anodes which passed current and exhibited moderate resistance to corrosive attack such anodes produced little or no sodium perchlorate.

Some experiments with nital passivated and lead dioxide coated anodes are also reported.

### II. GENERAL DISCUSSION

When we consider for the first time the problem of finding a substitute material for platinum in the manufacture of sodium perchlorate it is reasonable to start with an analysis of the behavior of platinum itself. We would expect this to lead to an understanding of all of the important factors governing the process. Based on a knowledge of these parameters we could then select other anode materials together with operating conditions that should prove good substitutes for platinum and the present process.

It has been a principle of considerable utility in electrochemical theory

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that among electrode processes which might occur the one with the lowest voltage does in fact occur. Of course, processes with only small differences in electrode voltage are expected to occur at the same time. In the production of perchlorate, as in other anode processes in water medium, oxygen evolution is the important competitor to the chlorate to perchlorate conversion process. The natural starting point in thinking about the behavior of platinum is a consideration of the anode voltages for the chlorate-perchlorate conversion and the water-oxygen conversion.

We have shown the calculation of these voltages in Appendix 1. Each working anode voltage comprises an equilibrium voltage and an over-voltage. It turns out that, under the conditions of interest to us, oxygen discharge should occur at -1.43 volts and perchlorate production at -2.54 volts. Thus, if the anode process here were determined by these voltages we would expect to obtain oxygen in the commercial cells and no perchlorate. In point of fact perchlorate forms and we must conclude that the process is not governed by the voltages calculated herewith.

A study of the literature shows that this is not a surprising situation. Hickling (15) cites well-known instances of this phenomenon of the higher voltage process occurring rather than oxygen evolution. The Kolbe reaction proceeds at an anode potential of -2.4 volts; the corresponding oxygen evolution potential is -2.0 volts. The Crum Brown-Walker synthesis goes at -2.8 volts; the oxygen potential is -2.0 volts. However, it would appear that instances of inorganic anode processes of this kind have not been previously pointed out. The chlorate-perchlorate case may have important implications for the theory of anode processes.

It would appear that electrochemical theory, particularly of anode processes, is in too primitive a state of development to be of much direct use

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to us in connection with the perchlorate anode problem. A preliminary analysis of the problem indicated to us that the material we sought must have a high oxygen over-voltage so that the oxygen discharge process would occur at a higher voltage than the perchlorate process. We see now that even this simple criterion is denied us, that the anode phenomena are too little understood to be interpreted in these simple terms.

In regard to the connection between electrode reactions and voltages, it has even been suggested that the anode potential was the result of the reaction taking place rather than the factor which determines which reaction shall go. Hickling (15) made this suggestion before the Faraday Society in 1947. The ensuing discussion (15) indicated mixed agreement and disagreement among the members present. The Hickling suggestion, as he admits, runs into the difficulty of explaining in a way satisfactory to electrochemical theory why a process giving rise to a high potential should take place in preference to one with a lower potential.

For our present purposes, the conclusion to be drawn from the foregoing is that the state of electrochemical science does not admit of a satisfactory theoretical approach to the perchlorate anode problem. If the theoretical line of development were to be pursued it would involve the support of much fundamental research in electrochemistry. Many laboratories would have to be involved and, in all probability, the work would take many years in accord with the usual pace of fundamental advances.

Consistent with the level of effort at Horizons a semi-empirical approach to the perchlorate anode problem was adopted. Reports of experimental findings in the literature provided possible starting points for further experimental work. The Pennsalt literature survey (1) clearly indicated that lead dioxide was the most promising material for further work. However, Pennsalt was

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intensively working in this area when Horizons entered the picture so that, to avoid duplication of effort, Horizons performed only a few scattered experiments with lead dioxide.

On the basis of the Pennsalt survey (1) the next most promising material appeared to be magnetite. There was reason to believe that materials such as molybdenum and titanium disilicide might serve as good anode materials. The experimental work at Horizons involved an intensive study of magnetite type materials and certain silicides. Some exploratory experiments were done with a variety of other materials also.

### III. MAGNETITE ANODES

An excellent survey of the literature relevant to the manufacture of perchlorate was completed by the Pennsylvania Salt Manufacturing Company in 1951 (1). This provided a good starting point for the work begun at Horizons in 1953. As mentioned previously it was evident from the survey that lead dioxide was a most promising material, and Pennsalt had been concentrating in that direction. Also, based on the survey, magnetite appeared to offer good prospects.

To quote from the review: "It appears, then, that magnetite electrodes with reasonably good mechanical strength and electrical properties can be made. The cost of such electrodes should not be prohibitive. It remains to be demonstrated, however, if a magnetite anode can actually be made to withstand the severe conditions existing in perchlorate manufacture." Magnetite has a history of successful usage in chlorate manufacture; the Pennsalt review quoted no successful application of the material to perchlorate manufacture.

The work of Howard (5) is alluded to in the Pennsalt literature review in connection with carborundum and high-silicon alloys (these being considered

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valueless as perchlorate anode materials). The review did not mention that the title of Howard's paper was "Oxygen Overvoltage of Artificial Magnetite in Chlorate Solutions". This work has important implications in connection with the possible use of magnetite as a perchlorate anode and deserves serious attention.

To quote from Howard's paper: "Attempts were made to oxidize sodium chlorate to perchlorate at a magnetite anode. Negative results were obtained. The oxygen overvoltage of a magnetite anode in N sodium chlorate was measured and found to be from 0.4 to 0.6 volt lower than that of smooth platinum. ..." "...It was known that an artificial magnetite had been used with success in some of the German alkali-chlorine cells, and we were anxious to test this material. Finally we obtained samples of such electrodes through the courtesy of the Chile Exploration Company. These artificial magnetite electrodes proved to be very resistant to corrosion, and in this respect appeared to offer a good substitute for platinum. Analysis of the electrolyte in which these anodes had been tested showed, however, that no perchlorate had been formed during the electrolysis, and this was found to be the case in all later experiments, even under the most favorable conditions for perchlorate formation, such as low temperature and higher current density. ..."

Ullmann (4) claims that magnetite anodes have not come into commercial use for perchlorate manufacture because they do not reach a high enough anode potential. However, an indication that perchlorate could in fact be produced at a magnetite anode was given in French Patent 704,325 (3) where it is stated that magnetite electrodes have not given as good results as platinum or graphite in sodium chlorate manufacture because they produce an appreciably greater proportion of perchlorate as the concentration of chlorate mounts.

Evidence that perchloric acid, at least, can be made at a magnetite anode

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is provided by U. S. Patent 1,271,633 (2). There it is claimed that platinum and fused magnetite were preferred to graphite as anodes for the electrolytic oxidation of chloric acid to perchloric acid.

Grebe (9) in a recent private communication indicated that magnetic iron oxide anodes were used for chlorate production many years ago. Since this statement was in a context of a discussion of the perchlorate problem it was assumed that chlorate was a typographical error and that perchlorate was really meant. In the light of the work of Howard and the body of experimental results obtained at Horizons it may be that no typographical error was made but that the statement about magnetite usage was intended to apply to chlorate manufacture. A clarification of this point by Dr. Grebe would be of some interest.

More recent work of Nagai (16) indicates that perchlorate can be made with magnetite anodes. This worker investigated the mechanism of perchlorate formation in the electrolysis of sodium chlorate with magnetite and platinum anodes. He reports that at high current densities the potential was higher for magnetite than platinum, and that the potential had no direct effect on the oxidation. Lacking access to the original paper it is difficult to interpret this last statement. Nagai concludes that the hydrogen peroxide theory of Glasstone concerning the catalytic decomposition of hydrogen peroxide and its effect on oxidation efficiency is valid.

#### Experimental

As reported previously, mixtures of ferric oxide, titanium oxide, and cupric oxide were calcined and fired at temperatures and in atmospheres calculated to transform the bodies to the magnetite structure. The resulting rods were tested as perchlorate anodes. We considered that the first requirement was for the body to stand up under bath attack and selected as our figure-

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of-merit the weight change of the anode. The ultimate requirement was, of course, that perchlorate be produced in practical current yield, and this was taken as the ultimate figure-of-merit.

For the early data on magnetite bodies reference is made to the project Technical Reports. Based on this data a selection was made of bodies that showed some promise and new specimens were made and tested. Table 1 gives the primary information concerning the tests.

In Table 1, for each specimen, appears the ceramic identification number and the weight percentages of the three components. Then the calcination and firing treatments are indicated. The record of ampere-hours passed through the cell is followed by the two figures-of-merit, the anode weight change and the current efficiency in grams sodium perchlorate per ampere-hour. Table 2 gives certain secondary information about the experiments.

The resistance to bath attack can be considered small only in the cases of K96-10BR and K96-12BR. However, the former was able to pass only 3.7 ampere-hours of electricity so the finding cannot be considered meaningful. K96-12BR, on the other hand, showed quite good resistance to oxidative attack and had 13.7 ampere-hours of charge passed through it, the largest for this set of anodes. This body contained 90% ferric oxide and 10% cupric oxide before firing, but no titanium dioxide; there appears to be a rough correlation indicating that the presence of titanium dioxide lowers the resistance of the anode to oxidative attack. We may consider that K96-12BR has met the first test and has satisfactory resistance to bath attack.

In regard to perchlorate production it is seen that all experiments gave disappointing results. Theoretical yield would be about 2.0 grams per ampere-hour. All efficiencies were on the order of 5 - 10% and must be rated as completely unsatisfactory.

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TABLE I

Magnetite Anodes  
Primary Information

Specimen Number	Percent by Weight			Treatment		Perchlorate Electrolysis		
	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CuO	Calcination	Firing*	Amp-Hr. Passed	Anode Wt. Change	g NaClO <sub>4</sub> per Amp-Hr.
K96-2AR	90	8	2	1900°F. 1 hr.	A	12.2	-6.44g.	0.21
K96-6CR	80	10	10	1700°F. 1 hr.	B	12.1	-8.162	0.14
K96-1AR	90	10	0	1900°F. 1 hr.	A	4.2	-10.011	none
K96-3AR	90	5	5	1900°F. 1 hr.	A	10.7	+0.665	none
K96-4BR	85	10	5	1900°F. 1 hr.	B	10.0	+0.524	0.17
K96-10BR	65	30	5	1900°F. 1 hr.	B	3.7	-0.050	none
K96-12BR	90	0	10	1700°F. 1 hr.	B	13.7	+0.176	0.12
K96-6BR	80	10	10	1700°F. 1 hr.	B	9.8	-6.689	0.15

\*Firing: A - 2200°F, 2 hrs., 97% A + 3% H<sub>2</sub>. B - 2200°F, 2 hrs., 82% H<sub>2</sub>O (v) + 17% N<sub>2</sub> + 0.8% H<sub>2</sub>.

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TABLE II

Magnetite Anodes  
Secondary Information

Specimen Number	Anode Number	Notebook References	Description After Firing (*)	Electrical Resistance	Grams NaCl Produced
K96-2AR	194-27	194-27, 31	A 14.5%	4.25 $\Omega$	0.99
K96-6CR	194-28	194-28, 31	A 13.8%	4.4 $\Omega$	0.20
K96-1AR	194-29	194-29, 40	C 15.7%	---	1.80
K96-3AR	194-30	194-30, 36	A 16 %	1.8 $\Omega$	0.35
K96-4BR	194-32	194-32,	A 10.5%	---	0.25
K96-10BR	194-33,	194-33,	D 12.5%	43.4 $\Omega$	0.23
K96-12BR	194-34	194-34,	E 13.8%	1.2 $\Omega$	0.19
K96-6BR	194-35	194-35,	A 12.5%	6.5 $\Omega$	0.58
K96-9CR	194-47	194-47, 49	B 6.0%	83 $\Omega$	---
K96-8CR	194-48	194-48, 49	B 8.4%	18 $\Omega$	---

\* A Vitrified, metallic appearance, took high polish

B Not completely vitrified

C Electrode surface cracked, vitrified

D Vitrified, badly warped

E Electrode broke during firing, vitrified

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Conclusion

We can produce a magnetite-type anode by pressing, calcination, firing and extrusion techniques. Such an anode can be perfected to stand up under the oxidative attack of the chlorate-perchlorate bath and pass electricity freely. However, perchlorate does not form appreciably on such an anode under our test conditions.

It is clear, of course, that additional study would offer some chance of learning what the parameters controlling perchlorate production at a magnetite anode were. Such parameters could then be subjected to control to enhance the yield.

IV. MAGNETITE-COATED ANODES

It was known that the magnetic oxide of iron, magnetite,  $\text{Fe}_3\text{O}_4$ , could be formed on the surface of iron by treatment with steam at high temperature. The preparation of magnetite anodes based on this principle was an attractive possibility. In a private communication previously alluded to (9) Grebe reported as follows.

"...the details of the best form of using magnetic iron oxide anodes for chlorate (sic!) production.

"Our experiments along this line many years ago were based on using a structure of ordinary iron welded together which was then exposed to steam at about 800 degrees C. which converted this iron into magnetite in the shape in which it is wanted.

"The unique results obtained in high temperature superheated steam may not be known to enough people so as to take advantage of magnetite electrodes as an alternative to platinum electrodes. ..."

There are a number of features of this communication worthy of discussion.

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First, Grebe's statement concerns chlorate production rather than perchlorate production. He may have meant this or a typographical error may be involved. In any case the possibility of use of magnetite produced in this way for perchlorate production was so promising that experimental study was justified.

Second, it is not clear whether the high temperature steam treatment produced a coating or whether the iron was converted to magnetite throughout its mass. Given suitable porosity on the part of the magnetite initially formed, it would appear possible to convert the iron to magnetite in some depth by prolonged exposure to steam. However, even if it is possible to effect a complete conversion to magnetite by thorough steaming, bodies produced by briefer treatment would consist of magnetite coated iron. Lacking proof to the contrary it would seem most reasonable to treat magnetite bodies prepared by the steaming technique as in the magnetite-coated category.

Third, Grebe specified the material steamed to be "ordinary iron". This implies that the exact nature of the basis substances is not too critical. However, it is well-known that relatively small quantities of other elements alter the properties of iron markedly, and it would be expected that such impurity or alloying ingredients would have an important effect on the character of a magnetite coating formed on a basis metal containing them. The success Grebe reported in the preparation of magnetite-coated chlorate anodes might well have been the result of a fortunate choice of the "ordinary iron" used in the process.

In any case, Horizons considered that there were good grounds to hope for a satisfactory material from the steaming technique. Our early work was done with the well-defined and reproducible material Armco Iron. Armco Iron is unusually pure ingot iron, containing approximately 0.1% carbon, 0.02% manganese, 0.005% phosphorus, and 0.025% sulfur. Short rods of Armco Iron were steamed at temperatures of the order of 800 degrees C. for varying periods

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of time. The magnetite coated bodies thereby produced were tested in small scale experiments entailing sodium chlorate electrolysis. Despite some scattered results of an apparently favorable nature no runs giving substantial perchlorate production were made so that they could be reproduced. Specimens that stood up to the oxidative attack of the bath were encountered. Details of these findings have been reported previously (18, 19).

Since satisfactory anodes did not result from treatment of pure iron with high temperature steam we thought that alloy irons and steels might work. On the one hand, the presence of the alloying elements would alter the nature of the magnetite coating, perhaps favorably. On the other, the basis metal might prove more stable to corrosive processes acting through the magnetite coating. It was considered that sometimes the coating would be porous and at other times rather coherent. Even if the latter were true corrosion of the basis metal could be expected to occur by such processes as cationic migration unless the nature of the metal was unfavorable for corrosion.

Another factor which we thought might have affected the behavior of the Armco Iron based anodes was that they were prepared in horizontal furnaces. This required that they rest on a side or end thereby preventing good access of steam to that area. In fact, it was observed that bath attack occurred most severely at just such areas. It was thought that this effect could be countered by using vertical furnaces for anode steaming with the body suspended to permit free access of steam to all regions. Vertical furnaces were constructed and used for this purpose.

#### Experimental

Information about magnetite-coated anodes prepared by treatment with high temperature steam in the vertical furnaces and not heretofore reported (19) is presented in Table 3. In each row of the table, following the product

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identification number, the material is briefly identified and the steam treatment indicated. Then the quantity of electricity passed through the cell in the process test, the quantity of sodium perchlorate produced per ampere-hour of charge, and a qualitative statement about the extent of anodic corrosion are given.

Numerous additional specimens of Armco Iron were steamed in the vertical furnace and process tested. Many of these stood up well against bath attack and permitted the passage of a good amount of current. No sodium perchlorate was produced at most of these anodes. A small amount of perchlorate was produced at anodes 186-38-2, 194-15-1, and 194-15-2. However, the latter two specimens suffered severe anodic corrosion. Even for 186-38-2 the current efficiency for perchlorate production was only about fifteen per cent.

A variety of other materials were put through the high-temperature steaming procedure as shown in the table. In practically all the experiments conducted the corrosion suffered in the chlorate-perchlorate bath was more severe with the material under test than with most of the plain Armco Iron based specimens. With anode 186-58-1 sodium perchlorate was produced at about 33% current efficiency. However, corrosion was so severe that only 6.7 ampere-hours of charge were passed through the cell in the process test. This was an iron-nickel alloy containing a rather high proportion of the alloying element and might provide a basis for further study since it was the most efficient perchlorate producer of the set.

#### Conclusions

It is possible to produce a magnetite coating on iron and steel rods by treatment with steam at high temperature; such specimens will permit ready passage of current and many will stand up well to oxidative attack when

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TABLE III

Magnetite-Coated Anodes

<u>Product Identification</u>	<u>Material</u>	<u>Steam Treatment</u>	<u>Electricity Passed Amp-Hr.</u>	<u>g NaClO<sub>4</sub>/ Amp-Hr.</u>	<u>Anode Weight Change</u>
186-4-1	Armco	800°C 1 hr.	12	cell broke no analysis	-3.726g
186-5-2	Armco	800°C 4 hrs.	11.3	none	-0.036g
186-6-2	Armco	1000°C 3 hrs.	13.1	none	+0.038g
186-4-2	Armco	800°C 1 hr.	8.8	none	---
186-5-1	Armco	800°C 4 hrs.	9.6	none	-0.038g
186-6-1	Armco	1000°C 3 hrs.	10	none	+0.105g
186-29-1	Armco	800-950°C 2 hrs.	9.8	none	-5.775g
186-29-2	Armco	800-950°C 2 hrs.	11.5	none	-5.225g
186-38-1	Armco	775-875°C 3 hrs.	4.87	---	-0.033g
186-38-2	Armco	775-875°C 3 hrs.	13.2	0.3	-0.182g
186-36-3	Armco	825-875°C 2.5 hrs.	9.7	none	-10.6g
186-36-4	Armco	825-875°C 2.5 hrs.	9.4	none	-10.6g
186-50-1	Nickel single crystals	875-900°C 2.5 hrs.	5.4	none	-2.09g
186-50-2	Nickel single crystals	875-900°C 3.7 hrs.	4	none	-3.11g
186-36-1	Armco	765-800°C 2.5 hrs. 885-900°C 2.5 hrs.	8.1	none	-15.62g
186-36-2	Armco	765-800°C 2.5 hrs. 875-900°C 3.7 hrs.	7.1	---	-15.94g
186-26-1	Armco	615-700°C 0.8 hrs.	9.3	none	-0.02g
186-26-2	Armco	615-700°C 0.8 hrs.	10.7	none	-0.03g
186-38-1A	Armco	775-875°C 3 hrs.	14.9	none	-0.40g
186-38-2A	Armco	775-875°C 3 hrs.	13.2	none	-0.74g

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TABLE III Cont.

Magnetite-Coated Anodes

<u>Product Identification</u>	<u>Material</u>	<u>Steam Treatment</u>	<u>Electricity Passed Amp-Hr.</u>	<u>g NaClO<sub>4</sub>/ Amp-Hr.</u>	<u>Anode Weight Change</u>
186-58-1	Iron (High Nickel)	870-900°C 5.5 hrs.	6.7	0.76	-6.27g
186-58-2	Nitralloy	870-900°C 5.5 hrs.	10.3	cell broken	-0.58g
186-62-1	Nitralloy	850-900°C 3.2 hrs.	13.1	—	-0.77g
186-62-2	Silicon Ferrite	850-900°C 3.2 hrs.	1.7	none	-2.53g
186-73-1	18-8 Stain- less T 304	875-925°C 1.8 hrs.	14.5	none	-8.83g
186-73-2	18-8 Stain- less T 321	875-925°C 1.8 hrs.	16.3	none	-10.06g
186-74-1	18.8 Stain- less 302	860-900°C 2 hrs.	14.7	none	-7.78g
186-74-2	Stainless 430	860-900°C 2 hrs.	4.3	none	-3.06g
186-75-1	CR Inconel 72 Ni, 15Cr, 7 Fe	900°C 3 hrs.	4.2	none	-2.61g
186-75-2	CR Incoloy 32 Ni, 21 Cr	900°C 3 hrs.	4.1	none	-3.02g
194-7-1	Stainless 430F	900°C 3 hrs.	3.5	none	-0.67g
194-7-2	99.4% Pure Nickel	900°C 3 hrs.	4.1	none	-5.23g
194-14-1	Cr Monel	900°C 3 hrs.	1.5	—	-3.64g
194-14-2	No. 410 Stain- less steel	900°C 3 hrs.	9.3	0.28	-1.60g
194-15-1	Armco	900°C 3 hrs.	8.5	0.19	-13.03g
194-15-2	Armco	900°C 3 hrs.	10.1	0.17	-11.65g
194-19-1	Nitralloy	850-950°C 6 hrs.	8.7	none	-0.75g
194-19-2	Nitralloy	850-950°C 6 hrs.	8.2	none	-1.26g

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tested as anodes in the electrolysis of sodium chlorate solutions. However, the production of sodium perchlorate is negligible under the standardized test conditions used in the experimental work at Horizons. Again it must be said that it is entirely possible that a more favorable selection of values for the several parameters that influence this electrolytic process could permit practical perchlorate production at the magnetite anode. There is no reason to think that the same set of conditions which are optimum for platinum are also best for magnetite.

#### V. NITAL PASSIVATED ANODES

Some of the considerations involved in the formation of a film or coating which confers corrosion protection upon its basis metal were discussed in an earlier report (18). A series of experiments was performed to see if treatment of Armco Iron with nital (8%  $\text{HNO}_3$  [Conc.] in 92% ethanol) had any possibility of producing a protective film that would resist attack as a perchlorate anode. Table 4 reports the results of such experiments not previously reported.

Opposite each product number appears a brief description of the nital treatment used. The total resistance of each anode is given; since the rods were roughly the same size differences in the resistance corresponds very roughly to differences in thickness of the nital-produced film. A description of the electrolysis follows comprising the initial and final volt-ampere level and the total charge passed through the cell in ampere-hours. In all cases considerable electricity was passed.

The column giving anode weight loss shows that no simple correlation between corrosion resistance and nital treatment was revealed by these experiments. In all cases perchlorate production was negligible.

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Conclusions

We were unable to produce satisfactory perchlorate anodes by nital treatments of Armco Iron.

VI. LEAD DIOXIDE-COATED ANODES

Kato and Koizumi (20) in 1934 reported the successful use of a coated lead dioxide anode in the preparation of perchlorate. Their basis material on which the coating was produced was graphite or nickel. Other materials were alluded to also but not specified. We considered it worthwhile to perform a few exploratory experiments in an attempt to produce a satisfactory coating on Armco Iron. Satisfactory results were not attained in the few experiments attempted.

The Armco Iron rods were cleaned first in acetone and then in 1:1 hydrochloric acid and methanol. The electrolyte for the plating operation consisted of a 30% solution of lead nitrate containing about 0.1% gelatin. The plating bath temperature was 50 degrees C. and several plating times were tried.

Table 5 contains the information about these experiments. The product number is followed by a brief statement of the plating treatment. The total resistance for each anode is shown but it does not correlate well with the coating thickness as judged by the extent of plating electrolysis. The conditions for the sodium chlorate electrolysis are given. As indicated, about 6.5 ampere-hours of electric charge were passed through the cells in each case.

Although the lead dioxide coated anodes stood up rather well under oxidative attack as indicated in the last column, no appreciable perchlorate formation was detected in the bath liquors.

Since the lead dioxide anode was a major interest of the Pennsylvania Salt Manufacturing Company under the Office of Naval Research program

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Horizons did no further work in the 1954.

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TABLE IV

Nital Passivated Armco Iron Anodes

Product Number	Treatment	Resistance	Electrolysis				Extent Amp-Hr.	Anode Weight Loss
			Start Volts	Start Amps.	Finish Volts	Finish Amps		
171-150-1	1 min. dip cold nital	8.5 m $\Omega$	5.1	2.4	4.1	1.8	13.2	-0.754g
171-150-2	3 min.	10 m $\Omega$	4.9	2.4	3.5	1.8	13.5	-0.412
171-150-3	10 min.	8.8 m $\Omega$	5.0	2.4	5.0	1.4	12.2	-0.230
171-150-4	none	39 m $\Omega$	5.0	2.4	4.3	1.6	13.8	-0.172
171-150-5	1 min. dip (unwashed)	415 m $\Omega$	5.1	2.4	5.1	2.2	12.8	-0.101
171-150-6	3 min. dip (unwashed)	56 m $\Omega$	4.9	2.4	4.4	2.5	13.2	-1.221

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TABLE V

## Lead Dioxide-Coated Armco Iron Anodes

Product Number	Treatment	Resistance	Electrolysis				Extent Amp-Hr.	Anode Weight Loss
			Start Volts	Amps	Volts	Finish Amps		
171-151-2	5 min. electrolysis at 50°C	320 m $\Omega$	4.8	2.4	3.2	0.2	6.5	-0.033g
171-151-3	15 min. electrolysis at 50°C	11 m $\Omega$	4.7	2.4	3.0	0.2	6.6	-0.045
171-151-4	1 min. electrolysis at 50°C	12 m $\Omega$	4.8	2.4	3.0	0.3	6.5	-0.050
171-151-6	60 min. electrolysis at 50°C	295 m $\Omega$	5.3	2.4	3.3	0.3	6.7	-0.078

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APPENDIX.

We calculate the Equilibrium and Over-Voltage for the evolution of oxygen and the production of perchlorate from chlorate for the conditions: pH = 6, 40 degrees C., 0.31 Amps./cm.<sup>2</sup>, and perchlorate-chlorate concentration ratio of 1:1.

O - Equilibrium Voltage

From Latimer (10)  $E^0 = -1.229$

Correction for pH = 6.  $0.059 \times 6 = 0.354$

Correction for t = 40.  $313/298 \times 0.354 = 0.372$

$-1.229 + 0.372 = -0.857$  volts

Result  $2H_2O = O_2 + 4H^+ (10^{-6}M) + 4e^-$ ,  $E_{40 \text{ deg. C}} = -0.857$

O - Over-Voltage

From Latimer (10) and Kohltoff and Sandell (13),  
eta = 0.4(5) at 0.023 amp./cm.<sup>2</sup>

From Stout (14),  
eta = constant +  $(2.3 RT/0.5 F) \log i$ .

The constant =  $0.45 + 0.19 = 0.64$

At 0.31 amp./cm.<sup>2</sup>. eta =  $0.64 + 0.118 \log 0.31$

Result eta = 0.57 volts (Temp correction negligible here).

ClO<sub>3</sub><sup>-</sup>/ClO<sub>4</sub><sup>-</sup> - Equilibrium Voltage

From Latimer (10)  $E^0 = -1.19$

Correction for pH = 6. 0.354 (as above)

Correction for t = 40. 0.372 (as above)

$-1.19 + 0.37 = -0.82$  volts

ClO<sub>3</sub><sup>-</sup>/ClO<sub>4</sub><sup>-</sup> - Over-Voltage

Hackett (8) determined this to be -1.72 volts

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List of References\*

1. Investigation of Methods to Produce Sodium Perchlorate Without the Use of Platinum. Part I. Literature Review.  
J. F. Goll, H. C. Miller, J. C. Grigger, F. D. Loomis, A. E. Lyden.  
Pennsylvania Salt Manufacturing Company, Wyndmoor, Pa. (Aug. 31, 1951)
2. U. S. Pat. 1,271,633 (July 9, 1918). E. C. Walker.
3. French Patent 704,325. (May 18, 1931). J. G. Farbenindustrie, A. G.
4. Ullmann, F., "Enzyklopädie der Technischen Chemie", Urban and Schwarzenberg, Berlin, Vol. III, 1929, pp. 299-307.
5. Howard, H. C., "Oxygen Overvoltage of Artificial Magnetite in Chlorate Solutions", Trans. Am. Electrochem. Soc., 43, 51-53 (1923)
6. Ishizaka, S. and Oki, K., "Overvoltage-measuring Apparatus and its Application to Oxygen Overvoltage", Repts. Govt. Chem. Ind. Research Inst. Tokyo, 47 187-95 (1952) (English summary) C. A. 47, 11050f (1953).
7. Balkanski, M., "The Overvoltage of Copper in a Solution of Cupric Phosphate and Phosphoric Acid in the Presence of Polyvinyl Alcohol", Compt. rend., 236, 2058-60(1953). C. A. 47, 11050g (1953).
8. Hackett, J. W., Status Report, Perchlorate Research NR 356-338, Contract Nonr-1213(00), August 1, 1953.
9. Letter by J. J. Grebe, Director, Nuclear Research and Development, Dow Chemical to L. W. Butz, Head, Chemistry Branch, Office of Naval Research, dated July 13, 1953.
10. Oxidation Potentials, 2nd Edition, W. M. Latimer, Prentice Hall 1952, page 56.
11. Textbook of Physical Chemistry, 2nd Edition, S. Glasstone, D. Van Nostrand, N. Y. (1946).
12. A. Hickling and S. Hill, "Oxygen Overvoltage. Part I...", pages 236-246 in Electrode Processes, A General Discussion of the Faraday Society, No. 1, London (1947).
13. Textbook of Quantitative Inorganic Analysis, J. M. Kolthoff and E. B. Sandell, Macmillan, N. Y. (1943). p. 153.
14. Stout, H. P., "The Energy of activation in the Electrodeposition of Oxygen", Ibid p. 246-7.
15. A. Hickling, "Some Anomalies in the Concept of Electrode Potential as the Determining Factor in the Occurrence of Anodic Reactions", pp. 227-9 in Electrode Processes, A General Discussion of the Faraday Society, No. 1, London (1947) See also pp 248-254.

\*When Chemical Abstract citation is given that is the form in which the reference was consulted.

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16. Nagai, T., "Electrolytic Manufacturing of Chlorate with Magnetite Anodes II. Perchlorate Formation", Proc. Fac. Eng., Keio Univ., 3, No. 8, 10 - 15 (1950). C. A. 3721 b 47 (1953).
17. Metals and Alloys Dictionary, M. Merlue-Sobel, Chemical Publishing Co., N. Y. (1944).
18. Finn, J. M., Technical Report, Anodes for Preparation of Alkali Perchlorates, Nos. 1 and 2, Horizons Incorporated, Cleveland, July 10, 1953.
19. Finn, J. M., Technical Report, Anodes for Preparation of Alkali Perchlorates, No. 3, Horizons Incorporated, Cleveland, October 23, 1953.
20. Katô, Y. and Koizumi, K., "A New Process for the Lead Peroxide Anode", J. Electrochem. Assoc. (Japan), 2, 309-12 (1934).

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